und Rb-Halogeniden (außer Fluoriden) beobachtete, typische Übergang zu sehr niedrigen Aktivierungsenthalpien bei hohen Temperaturen tritt also nicht auf[3,4]. Andererseits werden am Schmelzpunkt bei CsBr und CsI gegenüber anderen Alkalihalogeniden um 1 bis 2 Größenordnungen niedrigere Diffusionskoeffizienten gemessen.

Diese vorläufigen Ergebnisse lassen noch keine Angaben über den atomaren Mechanismus zu. Die gegenüber den übrigen Alkalihalogeniden veränderten geometrischen Verhältnisse (großer Edelgasradius, anderer Gittertyp) scheinen aber eine wichtige Rolle zu spielen.

Es ist beabsichtigt, noch weitere Messungen zur n-Dosisabhängigkeit durchzuführen und ergänzend die Transporteigenschaften in CsCl mit seinem Phasenübergang zu untersuchen.

Interdiffusion of ^{6}Li and ^{7}Li in Isotopically Nearly Pure Lithium Metal Melts

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(Z. Naturforschg. **22 a**, 2077—2080 [1967]; received 23 August 1967)

A capillary-reservoir technique has been used to investigate the interdiffusion of ^{6}Li and ^{7}Li in nearly pure (ca. 94%) ^{6}Li, as well as in nearly pure ^{7}Li. At the melting point the ratio of these diffusion coefficients is about 1.30. Extrapolation to tracer concentrations gives good qualitative agreement with the ratio of the viscosities of ^{7}Li and ^{6}Li. The interdiffusion coefficient ratio of the melts decreases with rising temperature, also in agreement with viscosity results. Quantum effects are likely to be responsible for the strong dependence on isotope mass.

Careful measurements by Ban, Randall and Montgomery[1] have shown that there is a very considerable difference in viscosity between isotopically pure liquid ^{6}Li and ^{7}Li. The ratio of the viscosity of ^{7}Li to that of ^{6}Li was found to be 1.44 at the melting point (about 180 °C), decreasing to 1.33 at 286 °C. This result, in striking contrast with the root-of-mass relationship expected on simple arguments, has hitherto not received a fully acceptable theoretical explanation. The surprising nature of the results of viscosity measurements motivates the inquiry, whether a similar isotope mass difference can be detected also in other transport properties.

The interdiffusion of the two Li-isotopes in liquid lithium of about natural composition has recently been measured between 196 and 440 °C [2], and it has been shown that a modified Stokes-Einstein formula, correlating self-diffusion with viscosity, is well obeyed. The purpose of the present work is to make a similar measurement in liquid lithium of reversed isotopic composition, i.e. to compare the results in nearly pure ^{6}Li with those in nearly pure ^{7}Li.

The capillary-reservoir arrangement described in ref.[2] was used also for the present investigation. Two slight modifications were made: a) the open capillary ends were turned upwards instead of downwards, thus reducing the risk of clogging the orifices with "skin" impurity in the reservoir; b) thermocouples were placed at several points of the bath and holder, permitting a more exact extrapolation to the temperature of the metal in the capillary and making sure of the absence of gravitational convection. The capillary diameter was 0.6 mm throughout.

For the ^{6}Li-rich metal a series of measurements was made at three different temperatures. Another series, at two temperatures, was made for the metal with natural composition, the reason being that it was not considered as sufficiently safe from systematic error to use the results of ref.[2] for the comparison, in view of the above-mentioned modifications. In this way both compositions were investigated under identical experimental conditions. Also, the earlier results could now be checked and the influence of the modifications assessed.

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In the first series, the capillaries were filled with lithium containing 91% ^{6}Li, produced by mixing metal enriched to 95,6% ^{6}Li, from Oak Ridge (99.95% chemically pure), with normal lithium from Koch-Light Co. (99.999% pure). The metal in the capillary was diffused into a reservoir, originally charged with the undiluted 95.6% ^{6}Li metal. The slight decrease (to some 94.8%) of the concentration in the reservoir during the course of the series was carefully kept check of. The mean concentration in the diffusion column during a diffusion run was 93% ^{6}Li.

The second (^{7}Li-rich) series was made with the same compositions as in ref.[2], i.e. diffusing metal with 92,5% ^{7}Li (99.999% pure Li) into a reservoir with 97% ^{7}Li (99.9% pure). The mean concentration in the capillaries during diffusion runs was 94.5% ^{7}Li.

The mass spectrometric analyses of the two series were performed at two separate periods, between which the ion source assembly was cleaned with special care, to avoid memory effects due to the great differences in isotopic composition.

The D-values were calculated and errors assessed with the same criteria as in ref.[2]. The results can be seen in Table 1 and Fig. 1.

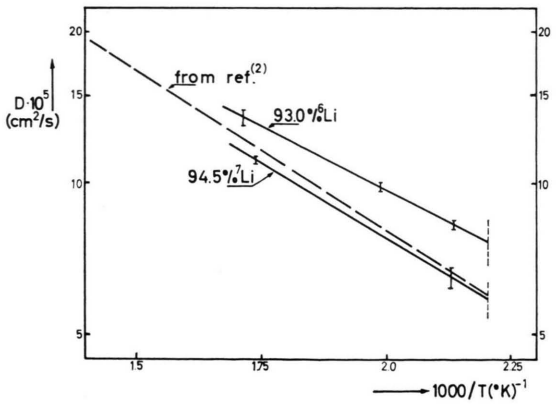

Fig. 1. Interdiffusion of ^{6}Li and ^{7}Li in isotopically nearly pure lithium melts.

Before discussing the diffusivity differences between the differently composed metals, it is of interest to see whether the results of ref.[2] are borne out by the present measurements. The 5 points for natural composition metal at 196 °C and 8 points at 302 °C can be used to compute the two parameters of the Arrhenius equation

$$D = D_0 \exp(-Q/RT), \qquad (1)$$

and the calculation yields $D_0 = (1.25 \pm 0.25) \times \times 10^{-3}$ cm^2/sec, and $Q = 2750 \pm 200$ cal/mole. This agrees satisfactorily with the results obtained in ref.[2], $D_0 = (1.41 \pm 0.12) \cdot 10^{-3}$ and $Q = 2825 \pm 90$. The agreement can also be seen in Fig. 1. The slight change in experimental set-up hardly at all affects the results at the lowest temperatures. At 300 °C, the slightly lower D-value obtained here as compared with the value obtained in ref.[2] may indicate the presence of a slight curvature in the true ARRHENIUS plot.

Table 2 shows the ratio of the diffusivity in the ^{6}Li rich metal to that in the ^{7}Li-rich metal at the melting point and at the highest temperature at which viscosities have been measured in ref.[1]. The

T(°C)	180.5 (m.p.)	286.0
$D_6 \cdot 10^5$	7.65 ± 0.15	12.50 ± 0.25
$D_6^* \cdot 10^5$ cm^2/s	7.80 ± 0.20	12.65 ± 0.25
$D_7 \cdot 10^5$	5.87 ± 0.30	10.50 ± 0.15
$D_7^* \cdot 10^5$ cm^2/s	5.75 ± 0.30	10.37 ± 0.15
η_6 (mP)	4.18 ± 0.05	3.49 ± 0.05
η_7 (mP)	6.00 ± 0.05	4.61 ± 0.05
D_6/D_7	1.30 ± 0.08	1.19 ± 0.03
D_6^*/D_7^* $(= q_D)$	1.35 ± 0.08	1.22 ± 0.035
η_7/η_6 $(= q_\eta)$	1.44 ± 0.02	1.33 ± 0.025
$q_\eta/q_D - 1$ (%)	6.3 ± 8.0	9.2 ± 5.0

Table 2. Comparison of isotope interdiffusion coefficients and of viscosities of almost pure ^{6}Li and ^{7}Li. The D-values (without asterisc) denote the present experimental results (see also Fig. 1). D^* are these results linearly extrapolated to zero tracer concentrations. η are the experimental viscosities[1].

% ^{6}Li	T(°C)	n	$10^5 D_{max}$	$10^5 D_{min}$	$10^5 D$	$10^5 \Delta D$
93.0 ± 0.7	195.0 ± 1.5	18	9.6	7.7	8.29	0.15
93.0 ± 0.7	229.0 ± 1.5	7	10.3	8.9	9.89	0.20
93.0 ± 0.7	310.5 ± 2.5	6	15.2	12.3	13.50	0.45
5.5 ± 0.7	196.0 ± 1.5	5	7.2	5.8	6.52	0.30
5.5 ± 0.7	302.0 ± 2.0	8	12.1	10.5	11.15	0.20

Table 1. *Experimental results.* The first column shows the computed average concentration during the course of a diffusion run. n denotes the number of capillaries (number of D measurements). The next two columns give the highest and lowest of the range of n D-values. The last two columns give the mean and the standard deviation. All D-values in cm^2/s.

D-values at these temperatures have been extrapolated and interpolated from Fig. 1. A linear extrapolation to zero concentrations, justified partly by its simplicity, partly by its success when used for viscosity[1], yields a ratio of the isotope interdiffusion coefficients D^* of pure ^{6}Li and ^{7}Li metals. As seen in Table 2, at both temperatures this ratio agrees quite well with the ratio of the viscosities η, as expected from a STOKES-EINSTEIN type formula[3, 2],

$$\eta \cdot D' = k\,T/r\,. \tag{2}$$

Here r is a geometric factor which only depends on atomic spacing; X-ray investigations of isotopically pure ^{6}Li and ^{7}Li[4] have shown that the lattice parameter is practically independent on isotopic mass. D' in formula 2 is, in principle, the ideal self-diffusion coefficient. This entity is very difficult to measure, unless the present accuracy of NMR or neutron scattering techniques is considerably improved. What has been measured here, i.e. the diffusion of ^{7}Li tracer in ^{6}Li and vice versa, is, however, adequate for a meaningful comparison, if it is taken into account that the region containing the tracer will adapt its vibration frequency somewhat to the differing mass of the tracer. The ratio of the tracer diffusion coefficients should thus be slightly less than that of the viscosities, as is observed to be the case in Table 2.

Now, evidence from several lines of investigation [5, 6, 7] suggests that atom transport in liquids takes place by the motion of coupled "clusters", rather than that of single atoms. In ref.[1] it is indeed suggested, that the size of the Li clusters may be sensitive to isotopic mass, and that the great departure from the simple $m^{\frac{1}{2}}$ law may in this way be accounted for. The viscosity ratio of 1.44 (instead of $\sqrt{7/6}$) would then mean that $\sqrt{n_7 \cdot 7/n_6 \cdot 6} = 1.44$, i.e. a ^{7}Li cluster contains on the average 1.8 times as many atoms as a ^{6}Li cluster. If one accepts this, and assumes the cluster size unaffected by the presence of tracer, each ^{7}Li tracer atom would have to share a cluster with $(n_6 - 1)$ ^{6}Li atoms, and each ^{6}Li tracer would move together with $(1.8\,n_6 - 1)$ ^{7}Li atoms. One would then expect

$$D_6^*/D_7^* = \left(\sqrt{\frac{6\,n_6}{1.8 \cdot 7\,n_6}} \Big/ \sqrt{\frac{6(n_6 - 1) + 7}{7(1.8\,n_6 - 1) + 6}}\right)(D_6'/D_7')\,, \tag{3}$$

which can be approximated into

$$\frac{D_6^*/D_7}{D_6'/D_7'} \cong 1 - \frac{1}{8.1\,n_6}\,. \tag{4}$$

The difference between D_6^*/D_7^* from the present measurements and D_6'/D_7' from the viscosity results at the m. p. might then be explained, if n_6 is about 1.8, n_7 about 3.3 atoms. The large uncertainty margin of the quotient on LHS does make this approach appear tentative at this temperature, but a better justified calculation for 286 °C gives $n_6 \cong 1.55$, $n_7 \cong 2.8$, with some 50% uncertainty.

This order of magnitude of n_7 is not unreasonable from the point of view of models suggested for the explanation of isotope effects in liquid metals subjected to potential or temperature gradients[8, 6]. However, one must not deduce too much significance from such a model in this case, until a more detailed discussion has been given of the actual physical mechanism that would cause the suggested isotope difference in cluster size.

It seems probable that the responsible mechanism is a quantum effect, as lithium is exceptional in two significant aspects: a) the ratio of the DEBYE temperature to the melting temperature is the highest of all metals, approaching indeed unity[9]; b) the atomic mass is the smallest of all metals. The first feature means that one may probably not neglect zero-point energy effects in diffusion. It is also likely that the DEBYE temperature of ^{6}Li is by some 30 °K higher than that of ^{7}Li (see, e.g., the LINDEMANN formula[10]). The second mentioned extreme property of Li, i.e. the low mass, makes it plausible that the two isotopes might obey different statistics on account of different spins, as has been thought to be the case e.g. for ^{3}He and ^{4}He[11]. According to rough estimate, the ratio of the DE BROGLIE wavelength to the interatomic distance of liquid Li is about one-fifteenth. This is smaller by about one order of magnitude than the correspond-

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ing ratio for liquid (non-superfluid) He, but considerably higher than for all other liquid metals. A confusing feature is, however, that in liquid He the even mass isotope possesses the greater viscosity, while the opposite is the case in Li. A rigorous theoretical treatment is certainly needed. If the DEBYE temperature criterium is the more important one, then in lithium below the melting point even greater isotopic differences should occur. Work is in progress at this laboratory to compare the tracer self-diffusion coefficients of solid ^{6}Li and ^{7}Li.

This research has been supported by Statens Naturvetenskapliga Forskningsråd and by Chalmerska Forskningsfonden. We are obliged to Drs. J. N. MUNDY, A. OTT and A. SJÖLANDER for interesting discussions. We thank ing. H. OLSSON for his able assistance at many stages of the work.

Farbzentren des Eisens als Ursache der Farbe von Amethyst

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(Z. Naturforschg. **22 a**, 2080—2085 [1967]; eingegangen am 3. August 1967)

Durch Elektronenspinresonanzuntersuchungen wurden drei Zentren dreiwertigen Eisens in Amethyst nachgewiesen: auf Si-Gitterplatz mit einem Alkali- oder Erdalkaliion auf benachbartem Zwischengitterplatz (S_1) bzw. mit einem Proton an einem der vier nächsten Sauerstoffatome (S_2) und ein völlig andersartiges Zentrum, das auf Grund optischer Absorptionsuntersuchungen als Zwischengitterion (I) gedeutet wird. Die Intensitätsänderungen dieser Zentren beim Bleichen und Verfärben des Amethysts lassen sich verstehen unter der Annahme, daß beim Verfärben S_1-Zentren zu vierwertigem Eisen oxydiert und ebenso viele I-Zentren zu zweiwertigem reduziert werden. Dabei entstehen S_2-Zentren aus S_1 als Nebenprodukt der Bestrahlung:

$$(x+y)\,\mathrm{Fe^{3+}(S_1)} + x\,\mathrm{Fe^{3+}(I)} \underset{T \geqq 300\,^\circ\mathrm{C}}{\overset{h\nu}{\rightleftharpoons}} x\,\mathrm{Fe^{4+}(S)} + x\,\mathrm{Fe^{2+}(I)} + y\,\mathrm{Fe^{3+}(S_2)}\,.$$

Eine ESR-Linie des Amethystzentrums wurde gefunden, die mit dieser Deutung in Einklang ist. Die Absorptionsbanden bei 545 und 357 nm werden als Elektronenüberführungsbanden $t_1(\pi) \rightarrow 2e$ und $t_1(\pi) \rightarrow 3t_2$ gedeutet. Eine eindeutige Zuordnung der schwächeren Kristallfeldbande bei 950 nm ist dagegen bisher nicht möglich. Für Fe^{4+} in tetraedrischer Anordnung ist eine Bande in diesem Spektralbereich zu erwarten, andererseits zeigt auch zweiwertiges Eisen in synthetischen Quarzen eine gleiche oder zumindest sehr ähnliche Bande. Ihre Lage erlaubt eine klare Entscheidung darüber, welcher von zwei möglichen Zwischengitterplätzen durch das zweiwertige Eisen und damit wahrscheinlich auch durch die I-Zentren des dreiwertigen besetzt wird.

Die Farbe von Amethyst ist lange Gegenstand von Vermutungen gewesen. HOLDEN[1] konnte 1925 zeigen, daß die Farbtiefe mit dem Eisengehalt wächst, seine sorgfältigen Untersuchungen zeigen aber auch, daß von einer streng quantitativen Beziehung keine Rede sein kann. Die Farbe ist thermisch instabil, die Aktivierungsenergie der Entfärbung ist mit 55 kcal/mol[2] praktisch gleich der Energie der optischen Anregung, die zu der Bande bei 545 nm führt. Auch UV-Licht bleicht Amethyst[3]. Bereits 1906 hatte BERTHELOT[4] gezeigt, daß radioaktive Strahlung einen solchen farblosen Amethyst wieder verfärbt, auch die Energie von RÖNTGEN-Strahlen reicht dazu aus. Bei Temperaturen oberhalb 350 °C wird Amethyst irreversibel gelb gefärbt in Bereichen, die vorher intensive Amethystfärbung aufwiesen. Dieser gelbe Amethyst gleicht dem in der Natur vorkommenden Citrin völlig; die meisten als Schmucksteine verwandten Citrine sind erhitzte Amethyste.

Die Entstehung der Färbung durch ionisierende Strahlung legt nahe, ein ungepaartes Elektron oder Defektelektron, delokalisiert über mehrere Sauerstoffatome ähnlich dem Rauchquarzzentrum[5], oder eine ungewöhnliche Wertigkeit des Eisens als Ursache der Färbung anzusehen.

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